[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

The Action of Silver-catalyzed Persulfate on 1,2-Glycols[1]

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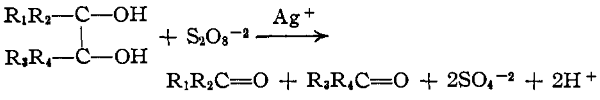
A new glycol splitting agent, silver-catalyzed persulfate, has been characterized for the first time. Glycol cleavage products, aldehydes, ketones or both, were obtained in moderately good to excellent yields (40–100%), dependent upon the specific glycol used. The reaction seems to be general for water-soluble glycols. Primary and secondary glycols averaged more than 1 mole of aldehyde product per mole of glycol, while a water-soluble tertiary glycol, pinacol, gave two moles of ketone per mole of glycol. α-Hydroxy ketones or α-hydroxy aldehydes were obtained in small amounts as co-products. Water-insoluble glycols were found to be either non-reactive or sluggish with the reagent. Optimum procedures developed for this reaction require the use of catalytic amounts of silver, 0.002–0.01 *M* Ag^+ concentration. Silver-catalyzed persulfate, unlike lead tetraacetate and periodic acid, is not specific for 1,2-glycols. Monohydric alcohols and aldehydes react readily with the reagent. The silver-catalyzed persulfate–glycol cleavage reaction has been analyzed in the light of mechanisms proposed for the action of periodic acid and lead tetraacetate. Kinetic studies on the reaction with *cis*- and *trans*-cyclohexanediols show strikingly identical rates of reaction for both isomers.

Heidt, Gladding and Purves, in a paper[3] devoted to a theoretical discussion of glycol cleavage reagents, analyzed structural requirements for oxidants capable of reacting similarly to potassium periodate[4] and lead tetraacetate.[5,6] On the basis of atomic distance, ionic size, valence changes of the central atom, oxidation potentials, and assuming Criegee's cyclic inner ester theory,[7a,b] of glycol splitting, they deduced that Ag^{+3}, or silver-catalyzed persulfate, amongst others, also should show glycol-splitting properties. Limited experimental data were given by the authors for the cleavage of ethylene glycol to formaldehyde with this reagent.

It was of interest to explore further the reaction of silver-catalyzed persulfates with glycols. We have treated silver-catalyzed persulfate with a variety of glycols, $R_1R_2\text{-C(OH)-C(OH)-}R_3R_4$, where R = alkyl, aryl, cycloalkyl or hydrogen. Glycol cleavage products, notably aldehydes and ketones, were obtained in moderately good to excellent yields (40–100%), dependent upon the specific glycol used (Table I). In general, primary and secondary glycols gave slightly more than one mole of aldehyde product per mole of glycol. Quantitative cleavage, two moles of ketone per mole of glycol, was obtained with a tertiary glycol, pinacol. Hydroxy ketones, resulting from a normal Fenton[8]-type oxidative attack on a single –CHOH– group also were obtained in small amount. Generally, the yield of such compounds was from 0 to 5%. *cis*- and *trans*-cyclohexanediol gave higher yields (10–12%) of the hydroxy ketone, 2-hydroxycyclohexanone along with the expected glycol cleavage product, adipdialdehyde.

Aldehyde and ketone products were dominant in all cases where a reaction was obtained, indicating the primary reaction to be of the type



$$\begin{array}{l} R_1R_2\text{—C—OH} \\ \quad\quad\;\; | \\ R_3R_4\text{—C—OH} \end{array} + S_2O_8^{-2} \xrightarrow{Ag^+} R_1R_2C{=}O + R_3R_4C{=}O + 2SO_4^{-2} + 2H^+$$

Water-insoluble glycols were found to be either completely non-reactive or sluggish with the reagent. Elevated temperatures, *e.g.*, 50–60°, were found helpful for increasing the reaction rates and raising the yields with slightly soluble glycols, *e.g.*, 4,5-octanediol. The use of non-aqueous media was generally unsuccessful. Free carboxy groups, *e.g.*, in 9,10-dihydroxystearic acid, interfered by precipitation of the silver catalyst as an insoluble silver salt. Compounds known to precipitate or complex Ag^+ must accordingly be absent.

Generally, 0.01–0.1 mole of reactants in dilute aqueous solution were employed in this study. The difficulty of isolating water-soluble lower aldehydes from dilute aqueous solution made it necessary to devise suitable quantitative procedures for following the progress of the reactions. Because α-hydroxy ketones were frequently co-products of the reaction, means also had to be devised for analytically distinguishing between their formation and that of the glycol cleavage products. The latter, in the case of primary and secondary glycols, were aldehydes. Separation, by way of derivatives, was effected here by use of "methon" reagent (5,5-dimethyldihydroresorcinol) for quantitative precipitation of the aldehyde products. Using 2,4-dinitrophenylhydrazine for precipitation of the total carbonyl product (both aldehydes and ketones), the respective aldehyde and α-hydroxy ketone content of the reaction products could be calculated. The analytical work was simplified by the choice, wherever possible, of symmetrical glycols for study, so that glycol cleavage would result in but a single product.

In moderate scale experiments with hydrobenzoin, phenylethylene glycol and pinacol, isolation of specific cleavage products as such was effected readily.

In the case of the oxidation of cyclohexanediol, a co-product was isolated and identified as the 2,4-dinitrophenylhydrazone of 2-hydroxycyclohexanone. α-Hydroxy ketones rather than 1,2-diketones are believed to be co-products of the action of sil-

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[2] Abstracted in part from a thesis submitted by F. P. Greenspan in partial fulfillment of the requirements for the Ph.D. degree. Buffalo Electro-Chemical Company, Inc., Division of Food Machinery and Chemical Corporation, Buffalo, N. Y.

[3] L. J. Heidt, E. K. Gladding and C. B. Purves, *Tappi Tech. Assoc. Papers*, **28**, 178 (1945).

[4] E. L. Jackson, "Periodic Acid Oxidation," in "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 341–375.

[5] R. Criegee, *Ber.*, **64**, 260 (1931).

[6] R. Criegee, *ibid.*, **65**, 1770 (1932).

[7] (a) R. Criegee, L. Kraft and B. Rank, *Ann.*, **507**, 159 (1933); (b) R. Criegee, *Angew. Chem.*, **53**, 321 (1940).

[8] H. J. Fenton and H. Jackson, *J. Chem. Soc.*, **75**, 1 (1899).

ver-catalyzed persulfate on glycols. An α-hydroxy ketone would be expected to give the same osazone, if formed, as the corresponding 1,2-diketone, so that identification of the precursor could not be made thereby.

Optimum reaction conditions were selected after a preliminary study of the variables affecting glycol cleavage with the reagent. Ethylene glycol and 2,3-butanediol were chosen as models for this work.

A 0.005–0.01 M concentration of Ag^+ was used for room temperature operations and 0.002 M for 50° operations, based upon kinetic studies of reaction rates with varying Ag^+ concentrations for the persulfate cleavage of ethylene glycol. These Ag^+ concentrations were calculated to give a rapid reaction (within 1 hour for ethylene glycol) combined with minimum decomposition of reagent. A 10% excess of persulfate reagent was commonly used for 30° reactions.

A study of yields of aldehyde as related to Ag^+ concentration for the 2,3-butanediol oxidation showed higher yields for 0.01 to 0.02 M Ag^+ than for 0.005 M Ag^+. Aldehyde yields for 0–5°, 30° and 50° reactions were lowest for the 0–5° reactions (Table II).

Increasing the glycol to persulfate ratio (use of excess glycol) resulted in a small increase of aldehyde yield with 2,3-butanediol (from 52 to 58%) with a significant increase for ethylene glycol (from 24 to 66%) (Table III).

From the equation for the reaction, it is obvious that the H^+ concentration increases during the reaction. Various buffered media were employed in an attempt to increase aldehyde yields, without success (Table IV).

Silver-catalyzed persulfate, unlike periodic acid and lead tetraacetate, cannot be classified as specific for 1,2-glycols. A substantial and rapid oxidation of primary and secondary alcohols was obtained (20–30% yields of aldehyde and ketone, respectively) at room temperatures. Water-soluble aldehydes, *e.g.*, acetaldehyde, were quantitatively oxidized by the silver-catalyzed persulfate under the very conditions used for glycol cleavage.

The ready reactivity of silver-catalyzed persulfate with aldehydes is a major factor in depressing the yields of aldehydes obtained from glycol cleavage. Kinetic studies of the Ag^+–persulfate reaction with cyclohexanediol (*cis* and *trans*) and 2,3-butanediol showed a rapid leveling off of aldehyde yield (based upon glycol used) at the 50% mark. Most significantly, the yield for the Ag^+–persulfate *trans*-cyclohexanediol reaction at 30 minutes was 85% of theory on the basis of persulfate actually consumed. Comparable results were obtained for 2,3-butanediol. Where the glycol cleavage product is a ketone, and as such resistant to further oxidation, yields have been quantitative, *e.g.*, pinacol.

The silver-catalyzed persulfate–glycol cleavage reaction has been analyzed in the light of mechanisms proposed for the action of periodic acid and lead tetraacetate. The Criegee proposal that an inner ester is formed by coördination of glycol with the central atom of the oxidant would require a faster reaction with a *cis*-glycol than with a *trans*-glycol.[9,10] This has been proved true for periodic acid[11a] and lead tetraacetate.[11b] The rate of reaction of silver-catalyzed persulfate with *trans*-cyclohexanediol was found to be identical with that for *cis*-cyclohexanediol. Accordingly, no experimental support has been found for the Criegee mechanism as applied to silver-catalyzed persulfate cleavage of glycols.

Since persulfates are known to form free radicals at room temperature, they provide an interesting test of Waters' free radical proposal for glycol cleavage.[12] If the silver-catalyzed persulfate–glycol cleavage proceeds through a free radical mechanism, glycol splitting should be observed similarly with persulfates alone, or in the presence of other oxidation–reduction systems, *e.g.*, Fe^{+2}, Cu^{+2}. No aldehyde formation could be detected in the reactions of 2,3-butanediol with persulfate, with and without Fe^{+2} and Cu^{+2} catalysts, even after prolonged reaction times.

On the basis of the experimental evidence, neither the Criegee inner ester theory nor the Waters free radical proposal appear applicable to the glycol-splitting action of silver-catalyzed persulfate.

The glycol cleavage reaction is not general for peroxy compounds but appears to be specific to persulfates. We have not found monopersulfuric acid or peracetic acid to cleave glycols in the presence of Ag^+.

Experimental

Materials.—Hydrobenzoin was prepared by reduction of benzoin with sodium amalgam. Benzopinacol was prepared by photochemical reduction with isopropyl alcohol.[13] *trans*-Cyclohexanediol was prepared by the action of performic acid on cyclohexene.[14] *cis*-Cyclohexanediol was prepared by low temperature oxidation of cyclohexene with permanganate using a modification of the procedure of Maan.[15] 10,11-Dihydroxyhendecanoic acid was prepared by the hydroxylation of undecylenic acid with 90% hydrogen peroxide and formic acid.[16] 1,2-Dodecanediol was prepared by hydroxylation of 1-dodecene.[17] Methyl 10,11-dihydroxyhendecanoate and methyl 9,10-dihydroxystearate were prepared by refluxing the respective dihydroxy acids with excess methanol in the presence of ethanesulfonic acid. 4,5-Octanediol was prepared by reduction of butyroin with lithium aluminum hydride in ether solution. All other reagents were commercial products recrystallized or distilled, wherever possible, prior to use.

Analytical

Determination of Total Carbonyl Groups.—Total carbonyl groups (ketone and aldehyde) were determined with 2,4-dinitrophenylhydrazine reagent using a modification of the procedure of Iddles, *et al.*[18]

Determination of Aldehydes.—Aldehydes were determined by precipitation of an aliquot of the reaction product with saturated methon (5,5-dimethyldihydroresorcinol) solution.[19]

Determination of α-Hydroxy Ketone in Presence of Aldehyde.—The general procedure was to analyze the re-

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(9) R. Criegee, L. Kraft and B. Rank, *Ann.*, **507**, 159 (1933).

(10) R. Criegee, *Angew. Chem.*, **53**, 321 (1940).

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(12) W. Waters, *Trans. Faraday Soc.*, **42**, 184 (1946).

(13) W. E. Bachmann, "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 71.

(14) J. English and J. D. Gregory, THIS JOURNAL, **69**, 2126 (1947).

(15) C. J. Maan, *Rec. trav. chim.*, **48**, 332 (1929).

(16) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

(17) D. Swern, G. N. Billen and J. T. Scanlan, THIS JOURNAL, **68**, 1504 (1946).

(18) H. A. Iddles, A. W. Low, R. D. Rosen and R. T. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

(19) D. Vorlander, *Z. anal. Chem.*, **77**, 321 (1929).

TABLE I

ACTION OF Ag^+ CATALYZED PERSULFATE ON VARIOUS GLYCOLS

Glycol	Molar ratio glycol to $K_2S_2O_8$	Products, yield,[a] % Aldehyde or ketone[b]	α-Hydroxy ketone[c]	Deriv. used for identcn. of cleavage prod.
Ethylene glycol	1:1	24.3	0.8[d]	2,4-Dinitrophenylhydrazone; dimethone
	10:1	60	6	
2,3-Butanediol	1:1	52	6.2	2,4-Dinitrophenylhydrazone; dimethone
	3:1	58	6	
Phenylethylene glycol	1:1	61[e]	...[f]	2,4-Dinitrophenylhydrazone
Hydrobenzoin (*meso*)	1:1	53.5[e]	...[f]	Dimethone
Pinacol	1:1	100[a] 87[e]	...[f]	2,4-Dinitrophenylhydrazone
Benzopinacol	1:1	0	0	
	1:2	0	0	
Cyclohexanediol (*trans*)	1:1	40.5	12.8	Dimethone
	3:1	55.0	4.0	2,4-Dinitrophenylhydrazone
Cyclohexanediol (*cis*)	1:1	40.5	10.4	Dimethone
4,5-Octanediol	1:1	28	...	Dimethone
	2:1	24	...	
	1:2	30.6	...	
	1:1 (50°)	38	0	
Diethyl tartrate	1:1	5.7		Not identified
10,11-Dihydroxyhendecanoic acid	1:1	No reaction		
1,2-Dodecanediol	1:1 (50°)	No reaction		
Methyl 9,10-dihydroxystearate	1:1 (50°)	No reaction		
Methyl 10,11-dihydroxyhendecanoate	1:1 (50°)	36.4	...	Not identified

[a] Unless otherwise noted, yields are based upon analysis of reaction products for small-scale experiments employing 0.01 mole of glycol, 0.01 mole of potassium persulfate and 0.01 *M* Ag^+ at room temperature. [b] Glycol cleavage product. [c] Fenton-type oxidation product. [d] Glycolaldehyde. [e] Yields based upon product isolated in moderate scale experiments. [f] Not determined.

action products for total carbonyl content and aldehydes as above. The dimethone value was then equated to the equivalent aldehyde hydrazone value and the latter subtracted from the total carbonyl found with 2,4-dinitrophenylhydrazine. The difference, assumed to be the corresponding osazone, gave the α-hydroxy ketone content.

In the case of ethylene glycol, the α-hydroxyaldehyde product was determined readily by precipitation with 2,4-dinitrophenylhydrazine, followed by hot ethanol (50 ml.) treatment of the dried and weighed precipitate. The ethanol insoluble portion was estimated as the glyoxal osazone.

For *cis*- and *trans*-cyclohexanediol, the 2-hydroxycyclohexanone co-product was determined on the basis of the solubility of the corresponding 2,4-dinitrophenylhydrazone in hot ethanol. The 2,4-dinitrophenylhydrazone of adipdialdehyde was found to be insoluble in this solvent, thus making ready separation possible.

Determination of Persulfate.—Analysis for persulfate was performed by a standard procedure[20] except that ceric sulfate was employed for the back titration of ferrous ammonium sulfate.

Procedures

Oxidation of 2,3-Butanediol.—The oxidation of 2,3-butanediol with silver-catalyzed persulfate is typical of the procedure employed for glycols, yielding water-soluble cleavage products. Results for the various glycols studied are in Table I.

To 110 ml. of an 0.1 *M* solution of potassium persulfate (10% excess) was added 0.9660 g. (0.01 mole) of 2,3-butanediol, followed by 1.7 ml. of a 10% silver nitrate solution. The resultant solution (0.01 *M* Ag^+) was stirred for 2 hours without cooling, at which time an analysis for residual persulfate showed the reaction to be complete. The temperature rose to approximately 32° during this period.

One gram of sodium chloride was added to the reaction products and the resultant silver chloride filtered. A 5-ml. aliquot of the filtrate was added slowly with stirring to 70 ml. of the 2,4-dinitrophenylhydrazine reagent and gave 0.1109 g. of a yellow 2,4-dinitrophenylhydrazone. Repeated recrystallizations from ethyl acetate yielded a bright yellow solid melting at 167–167.5° (m.p. for the 2,4-dinitrophenylhydrazone of acetaldehyde, 168°).[21]

A separate 5-ml. aliquot of the reaction product gave with "methon reagent" 0.1221 g. of white acetaldimethone. Recrystallization from an ethanol–water mixture gave a white product melting at 139° (m.p. for acetaldimethone 139°).[21] Applying a solubility correction (see "Analytical") to the acetaldimethone, this was equivalent to a total yield of 0.458 g. of acetaldehyde or 52% of theory. On the basis of the total carbonyl assay above, the non-aldehyde carbonyl fraction was accordingly 0.0123 g. of a 2,4-dinitrophenylhydrazone. This calculated as 3-hydroxy-2-butanone (acetoin) corresponded to a total yield of 0.053 g. or 6.2%.

With a 0.005 *M* Ag^+ concentration, the yields were 41% acetaldehyde and 9.7% acetoin. With 0.02 *M* Ag^+, the acetaldehyde yield was 51% with no acetoin. A saturated silver sulfate solution gave 47% acetaldehyde with no acetoin.

When 3 moles of persulfate were used to 1 mole of glycol, 15% acetic acid was obtained as a product.

Oxidation of Phenylethylene Glycol.—The oxidation of phenylethylene glycol is typical of the moderate scale experiments (Table I) run with glycols yielding water-insoluble aldehydes or ketones.

Potassium persulfate, 29.7 g. (0.11 mole), was added with stirring to 13.8 g. of phenylethylene glycol (0.1 mole) in 300 ml. of water. One and three-tenths ml. of a 10% silver nitrate solution was then added to this mixture at 30°. Stirring was maintained throughout. Within one hour, the temperature rose to 40° and a yellow oil, smelling strongly of benzaldehyde, separated from the solution.

A persulfate analysis showed the reaction to be practically complete at this point. The flask contents were accordingly steam distilled, in an all-glass steam distillation apparatus, until the distillate coming over was clear. Total distillate collected was 125 ml. consisting of an aqueous upper layer and a colorless oil. The distillate was extracted with ether three times and the extract dried with anhydrous sodium sulfate. After filtration, the ether was removed in a dry nitrogen stream giving 6.5 g. of benzaldehyde, equiva-

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(20) N. H. Furman, "Scott's Standard Methods of Analysis," D. Von Nostrand Co., Inc., New York, N. Y., 1938, p. 922.

(21) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

lent to 61.4% of theory. Preparation of the corresponding dimethone gave a white benzaldimethone which, on recrystallization from ethanol, melted at 192–193° (m.p. 193°[21]). 2,4-Dinitrophenylhydrazine gave an orange benzaldehyde hydrazone, m.p. 236–236.5° (m.p., 237°[21]).

Oxidation of Pinacol.—Pinacol hydrate (22.6 g., 0.1 mole) dissolved in 200 ml. of water treated with vigorous stirring at 50°, with 32.4 g. of potassium persulfate (0.12 mole), followed by 1.76 ml. of a 10% silver nitrate solution (Ag^+ concentration, 0.004 *M*). After one hour, the reaction mixture was cooled. A 1-ml. aliquot (1.0799 g.) of the reaction products added to 2,4-dinitrophenylhydrazine gave 0.2024 g. of the acetone 2,4-dinitrophenylhydrazone, equivalent to a total yield of 11.6 g. of acetone or 100% of theory. Repeated recrystallizations from ethyl acetate gave a product melting at 127.5–128° (m.p. for acetone 2,4-dinitrophenylhydrazone, 128°[21]).

The balance of the reaction mixture was distilled through a 1-foot Vigreux column topped by a variable take-off. With a reflux ratio, pot-to-distillate, of 10-to-1, 8.0 g. of a fraction boiling at 55.5–56.0° at 759 mm. was collected. This was equivalent to a yield of 86.5%.

Variables Affecting the Silver-catalyzed Persulfate–Glycol Reaction.—A number of reaction variables were studied for the oxidations of 2,3-butanediol and ethylene glycol. The procedure was the same as that detailed under 2,3-butanediol above. The effect of temperature on product yields is shown in Table II. The influence of varying molar ratios of glycol to persulfate is given in Table III. The effect of *p*H on the silver-catalyzed persulfate glycol reaction is shown in Table IV.

TABLE II

EFFECT OF TEMPERATURE ON SILVER–PERSULFATE–GLYCOL REACTION

	Temp., °C.	Product yield, % Aldehyde	Product yield, % α-Hydroxy ketone
2,3-Butanediol	0–5	43.2[b]	0
	25	52.0[a]	6.2
	50	48.5[a]	0.3
Ethylene glycol	0–5	16.8[b]	3.4[c]
	25	24.0[a]	1.5[c]

[a] Reaction time of 3 hours. [b] Reaction time of 42 hours. [c] Actually an α-hydroxy aldehyde, glycol aldehyde.

TABLE III

EFFECT OF GLYCOL TO PERSULFATE RATIO ON SILVER–PERSULFATE–GLYCOL REACTION

	Molar ratio glycol to $K_2S_2O_8$	Yields, % Aldehyde	Yields, % α-Hydroxy ketone
2,3-Butanediol	1:1	52.0	6.2
	3:1	58.0	6.0
	10:1	58.0	7.0
	1:3	..[b]	..[b]
Ethylene glycol	1:1	24.0	1.5
	3:1	53.0	4.0
	10:1	59–66[a]	11–19[a]
	1:3	0.3[b]	....

[a] Different runs. [b] 15–20% yields of carboxy acid corresponding to the aldehyde oxidation product were obtained.

The Action of Silver-catalyzed Persulfate on Other Functional Groups.—The action of silver catalyzed persulfate on *n*-butyl and *sec*-butyl alcohols was studied utilizing 0.01 mole of the respective alcohols and persulfate in the presence of 0.1 *M* Ag^+.

n-Butyl alcohol was oxidized to butyraldehyde with a yield of 20.3%. Oxidation of *sec*-butyl alcohol gave 31.5% of isobutyraldehyde.

When acetaldehyde was treated with potassium persulfate in the presence of silver ion catalyst, all of the aldehyde was oxidized (a 2,4-dinitrophenylhydrazine test was negative) and acetic acid was noted as a product.

Action of Silver-catalyzed Peracids on 1,2-Glycols.—The action of peracetic acid and monopersulfuric acid on 1,2-glycols was studied, utilizing 0.01–0.1 mole of glycol (ethylene glycol and hydrobenzoin) and 0.1 mole of peracid and 0.1 *M* Ag^+. Procedural details were the same as described for 2,3-butanediol. Aldehyde tests were negative in all cases. Little or no consumption of peracetic acid could be detected for the ethylene glycol–peracetic acid over the course of 1 hour at 30°. Hydrobenzoin was recovered unchanged after 24 hours from the peracetic acid–hydrobenzoin reaction.

TABLE IV

EFFECT OF "*p*H" ON SILVER–PERSULFATE–GLYCOL REACTION

Buffer	*p*H	Yields, % Aldehyde	Yields, % α-Hydroxy ketone
2,3-Butanediol–			
1 *M* Acetate–acetic	4.6	40.0	0
2 *M* Acetic	2.2	44.3	0
1 *M* Sulfuric	0	43.5	5.0
1 *M* Borate–borax	7.6	20.6	1.9
No buffer	3.4 (init.)	52.0	6.2
Ethylene glycol–			
1 *M* Acetate–acetic	4.6	9.7	1.9
1 *M* Borate–borax	7.0–7.6	20	2.5
1 *M* Sulfuric acid	0	31	0.4
No buffer	3.4 (init.)	24	1.5

Reaction Mechanism Studies

Kinetics of the Silver-catalyzed Persulfate Reaction with *cis*- and *trans*-Cyclohexanediol.—A 1.16-g. sample (0.01 mole) each of *cis*- and *trans*-cyclohexanediol was separately dissolved in 100 ml. of an 0.1 *M* potassium persulfate (0.01 mole) solution contained in 100-ml. volumetric flasks and treated in identical fashion thereafter. The flasks were placed in a thermostated bath at 30° and allowed to come to temperature equilibrium (15 minutes with occasional shaking). To the glycol solution was then added 1.7 ml. of a 10% silver nitrate (0.01 *M* final Ag^+ concentration) to initiate the reaction. Two 5-ml. aliquots were withdrawn at given intervals over the course of 4 hours for (a) determination of persulfate reacted and (b) determination of carbonyl content by precipitation with 2,4-dinitrophenylhydrazine. A blank consisting of 1.7 ml. of 10% silver nitrate in 100 ml. of 0.1 *M* potassium persulfate was run simultaneously. Figure 1 shows a plot of the kinetics of the reaction with the *cis* and *trans* isomers.

Action of Various Persulfate Oxidation–Reduction Systems on 1,2-Glycols.—To each of 4 flasks was added 0.9 g. of 2,3-butanediol. To flasks 2, 3 and 4 were added 110 ml. of 0.1 *M* potassium persulfate (0.11 mole). Flask 1 received 120 ml. of the same reagent (0.12 mole). Cu^{++} catalyst, 0.02 and 0.1 *M*, were added to flasks 2 and 3, respectively. Fe^{++} catalyst (0.02 *M*) was added to flask 4. No catalyst was added to flask 1. The flasks were stoppered and stored at room temperatures. Aldehyde tests were made at 2, 11 and 16 days with fuschin and "methon" reagents. For the latter, an aliquot was adjusted to *p*H 6 and filtered free of precipitated metallic hydroxide after Celite addition.

Very little persulfate consumption was noted in flasks 1, 2 and 3 over a 2-day period. Aldehyde tests were negative over the 16-day interval. Appreciable persulfate consumption was shown in

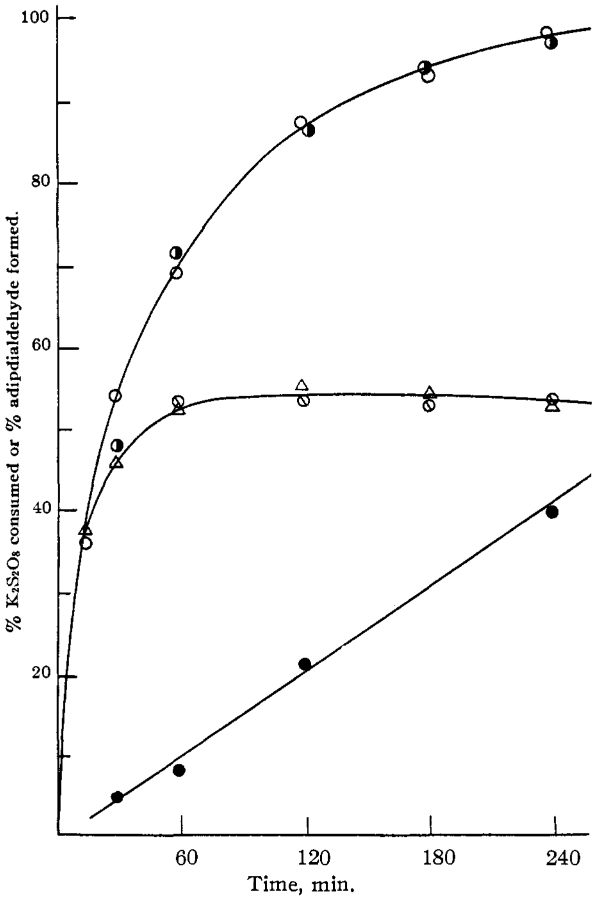

Fig. 1.—Kinetics of Ag^+–$K_2S_2O_8$ action on *cis*- and *trans*-cyclohexane diol: ○, $S_2O_8^{-2}$ consumption, *trans*-diol; ◑, $S_2O_8^{-2}$ consumption, *cis*-diol; ⊘, CO yield, *cis*-diol; △, CO yield, *trans*-diol; ●, $S_2O_8^{-2}$ consumption blank.

flask 4. The fuchsin–aldehyde and methon reagent tests were negative. Positive carbonyl tests with 2,4-dinitrophenylhydrazine and Tollens reagent indicated the presence of an α-hydroxy ketone. A quantitative assay at 16 days with the former reagent gave a 28% yield of α-hydroxyketone calculated as acetoin. This represents as far as known the first demonstration of a Fenton-type oxidation of a glycol with a persulfate and is under further investigation.

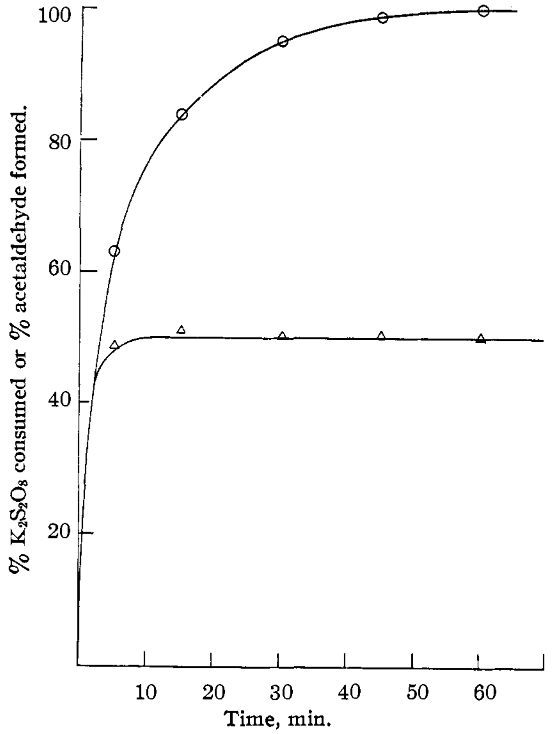

Fig. 2.—Kinetics of Ag^+–$K_2S_2O_8$ action on 2,3-butanediol: ○, $S_2O_8^{-2}$ consumption; △, CO yield.

Kinetics of the Silver-catalyzed Persulfate Reaction with 2,3-Butanediol.—Kinetic studies were made of the Ag^+–persulfate–butanediol reaction utilizing 0.01 mole reactants and 0.01 *M* Ag^+. The procedure was the same as that described above for cyclohexanediol. Results are shown in Fig. 2.

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